



PATENT SPECIFICATION

722,184

Date of filing Complete Specification Dec. 4, 1952.

Application Date Sept. 4, 1951.

No. 20894/51.

Complete Specification Published Jan. 19, 1955.

Index at acceptance:—Class 82(1), 14A2, 14A3(B: C), 14A4C, P3.

COMPLETE SPECIFICATION

Improvements in or relating to the production of Pure Titanium and Zirconium

We, JOSEPH PEPPO LEVY, a Turkish Citizen, of 1, Kathleen Avenue, Acton, London, W.3, DAVID HARRY PICKARD and LIONEL PICKARD, both British Subjects, and both of 223, St. John Street, London, E.C.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of titanium or zirconium metal in a high state of purity.

Titanium and zirconium are readily produced in the form of volatilizable chlorides by direct reduction of their ores with carbon in the presence of chlorine, but the production of the pure metal from the tetrachlorides is a matter of considerable difficulty owing to the great affinity of these metals for other substances, more particularly to their affinity for both the oxygen and nitrogen of the atmosphere, and for carbon and hydrogen. Even traces of impurities, particularly oxygen and nitrogen, may render the metal brittle and unworkable and of much less commercial value, although the metal is of great utility when in the pure condition.

Many processes have previously been suggested for obtaining pure titanium from the tetrachloride. Thus, it has been previously suggested to obtain titanium by reacting magnesium with titanium tetrachloride in accordance with the formula $2\text{Mg} + \text{TiCl}_4 = 2\text{MgCl}_2 + \text{Ti}$ by introducing the titanium chloride vapour into molten magnesium, titanium being retained in a matrix of unreacted magnesium and magnesium chloride. It is extremely difficult, however, if not impossible, to remove all occluded titanium tetrachloride vapour, and in the subsequent leaching of the mass with water to remove magnesium chloride, this residual tetrachloride vapour is hydrolysed, giving insoluble oxides and oxychlorides which cannot be subsequently removed without attacking the titanium itself. Moreover, the leaching itself is a difficult operation to carry to completion and the titanium obtained by this process usually con-

tains at least 1% of impurities, mainly because of the difficulty of leaching the solid matrix. The use of hydrochloric acid to remove unreacted magnesium may also introduce fresh impurities, since the hydrogen liberated may also act on very finely-divided titanium to form titanium hydride and impurities in the material normally used for lining the chamber may introduce further impurities which contaminate the titanium.

It has now been found that titanium and zirconium can be produced in a high state of purity without encountering the difficulties above referred to if the reduction reaction is carried out in the vapour phase in the presence of an inert gas (viz. one of the noble gases, in particular argon, helium or neon, on account of their availability) to act as an entrainment and effect the rapid removal and separation of the products of reaction.

It is also desirable, in order to avoid contamination by the walls of the reaction vessel of the titanium or zirconium metal when formed, to arrange for the reaction to take place in a reaction zone surrounded by moving inert gas and to carry away rapidly the reaction products as soon as formed to a cool zone without contact while hot with the walls of the vessel, and also to prevent mist particles of alkaline earth chloride from coalescing.

It will be shown hereinafter that the employment of a vapour phase reaction in conjunction with a moving inert gas entrainment not only avoids the difficulties hitherto encountered in obtaining pure metal, but also carries with it many advantages which could not have been foreseen.

Accordingly, in its broadest aspect, the present invention includes the process for the production of pure titanium or zirconium which comprises reacting the tetrachloride of the required metal in the vapour phase and in the presence of a moving inert gas with magnesium vapour, and passing the reaction products while entrained in the inert gas, through a zone sufficiently cool to solidify the magnesium chloride before the particles are allowed to settle.

The inert gas which may conveniently be

- argon on account of its availability is preferably employed as a vehicle to carry one or both of the reaction ingredients into the reaction zone as well as to carry the reaction products rapidly away from the reaction zone. The products of reaction are thus maintained in a finely-divided state in suspension until cool enough to be collected as a fine powder, and it is this feature of the invention which enables the titanium or zirconium metal to be separated from the magnesium chloride without the difficulties referred to above. Moreover, the inert gas acts to dilute the reaction ingredients and thereby enables the strongly exothermic reaction to be better controlled. It also sweeps away excess tetrachloride vapour and this is one of the many advantages of the use of a vapour phase reaction in conjunction with the employment of a moving inert gas. The higher temperature of the reaction provides a condition of greatly increased chemical activity. Furthermore, by reducing the tetrachloride with magnesium vapour, the reaction becomes practically quantitative, because at that temperature the products of reaction Ti or Zr+MgCl₂ are in the solid and liquid phases respectively and can thus be easily carried away by the entraining inert gas. This removal of the reaction products as rapidly as they are formed ensures that the reaction proceeds to completion and all the metal vapour is consumed leaving no residual matrix to be dissolved out as when conducting the reduction in the liquid phase. Furthermore, as will be shown hereinafter, the vapour phase reaction using an entraining gas enables a continuous process in a closed cycle to be carried out.
- In carrying out the invention, using the inert gas as a vehicle to carry the magnesium vapour forward, it may be caused to draw the vapour from a pool of boiling metal in a vessel surrounding the reaction vessel by passing it through a venturi and into the reaction vessel to meet a current of titanium or zirconium tetrachloride vapour. Ideal conditions obtain when the magnesium and the tetrachloride are in stoichiometric proportions, but a small excess of either reactant can be tolerated, and a slight excess of tetrachloride vapour over that required to maintain molar proportions prevents the tetrachloride vapour from striking back and acting on the surface of the pool of boiling magnesium. Any reaction of the surface of the molten magnesium makes it necessary to separate and recover the products of such reaction, with all the disadvantages hereinbefore mentioned. The inert gas passing through the venturi exerts a pumping action which carries the magnesium vapour into the reaction vessel very effectively.
- The reaction is strongly exothermic and the radiated heat may be utilised in maintaining the magnesium in a state of ebullition.
- The products of the reaction are obtained

in this way in the form of a finely-divided powder consisting of magnesium chloride and titanium or zirconium metal.

The deposition of both products of reaction in the form of a powder enables the metal to be extracted without difficulty. The reaction products do not come into contact with any wall surface until they are cool enough to remain uncontaminated.

Although argon is a comparatively expensive gas, very little is lost in the process, as the argon upon performing its function may be re-circulated after passing through condensers and heat exchangers which cool the gas and remove from it any excess tetrachloride. Thus, only small proportions of gas require to be introduced into the circuit from time to time to make good small losses which may occur.

In view of the necessity for keeping the molten magnesium out of contact with either oxygen or nitrogen of the atmosphere, the magnesium boiler may be fed with molten magnesium from a second heated vessel which is replenished by billets of solid metal. The tetrachloride is pressure-fed from a series of replenished storage tanks and the products of reaction are removed through an argon lock at convenient intervals without stopping the reaction.

The magnesium chloride can be easily removed and recovered from the titanium or zirconium metal in a condition which enables it to be economically returned to electrolytic cells for decomposition into metal and chlorine, both of which can be re-used in the process.

One specific method of carrying out the invention for the production of titanium in a continuous manner will now be described with reference to the accompanying drawing, which shows diagrammatically a form of reaction vessel with its accompanying melting vessel for supplying molten magnesium.

In the drawing the reaction vessel 10 is in the form of a cylinder, the sides of which at the top converge into the venturi throat 11, the upper part of the reaction vessel 10 being surrounded by concentric vessel 12 provided with a cover 13 which may be secured to the flange 14 by bolts (not shown) or otherwise. The reaction vessel is provided with a side inlet 15 passing through the outer vessel 12. Above the outer vessel 12 is a small box 16, provided with an inlet 17 and cover 19, through the bottom of which passes a tube 20 extending upwardly nearly to the top of the box 16 and downwardly through an aperture in the lid 13 terminating in a nozzle 21 situated centrally above the venturi throat 11. The outer vessel 12 communicates through the tube 22 near the bottom thereof with the bottom part of a melting vessel 23 closed with cover 24 in which is provided an inlet 25 of sufficient width to take billets of magnesium. The inlet 25 is closed with a cover 26. The

reaction vessel 10 is flanged at the bottom and attached to the wide cooling vessel 27 which is flanged top and bottom and the bottom flanged at 29 is bolted to the flanged inlet conduit 28 of the receiver 30 which has a narrower flanged outlet 31 bolted at 32 to the conduit 33 leading to an outlet 34 in the side of the cooling vessel 27. By means of the valves 35, 36, 37, 38 and 39, the receiver can be shut off from the rest of the apparatus for the purpose of uncoupling the receiver and changing it without opening it or the apparatus to communication with the outside atmosphere.

In operation the outer vessel 12 and the melting vessel 23 are enclosed in furnaces (not shown) which melt the magnesium metal introduced into the opening 26 and maintain the metal in 23 in a molten condition and that in the outer vessel 12 at the boiling point. The apparatus may be worked as a continuous process in which argon from a suitable storage is pumped into the box 16 at the inlet 17 and passes through a quantity of metallic calcium or other gettering material 18 and enters the outer vessel 12 through the delivery tube 20 and jet 21. The stream of argon emerging from the jet 21 and from thence into the venturi throat 11 sets up a pumping action which draws magnesium vapour from above the magnesium in the vessel 12 and carries it down the reaction vessel 10 where it meets a stream of titanium tetrachloride which enters through the inlet 15. An intense exothermic reaction is set up in the centre part of the reaction vessel 10 forming fine particles of titanium metal and a mist of magnesium chloride which is carried downwards and enters the cool zone 27 in the lower part of the apparatus where the magnesium chloride solidifies in powder form and the mixed powders are collected in the receiver 30. Argon containing excess tetrachloride passes out at 31 and enters a system of condensers for the removal of titanium tetrachloride which is passed to a suitable storage and the argon is re-circulated entering the apparatus again at 17. By closing the valves 35, 36, 37 and 38 and opening valve 39, the receiver may be changed periodically by undoing the attachments at 32 and 29, the argon circulation being uninterrupted through the short-circuiting valve 39.

The level of the molten magnesium in the outer vessel 12 is kept constant by addition of magnesium billets through the inlet 25 and the connection 22 enables molten magnesium to flow freely into the outer vessel 12 without air entering the apparatus.

The following is an example of an experimental batch carried out in an apparatus as above described:—

A gas-fired furnace was arranged to pre-melt billets of magnesium in the melting vessel 23 which could conveniently transfer

the molten metal at about 850° C. to the boiler 12 heated in a second similar furnace. 10 pounds of metal was contained in the magnesium boiler 12, the surface reaching to just below the venturi throat 11 which had a 70 diameter of $\frac{1}{16}$ ". The nozzle 21 having a diameter of $\frac{1}{16}$ " was situated above the venturi at a distance suitable for drawing into the reaction vessel magnesium vapour by the argon which is passed through it. The argon flow rate was $\frac{3}{4}$ cubic feet per minute and the magnesium evaporation was 8 pounds per hour. The titanium tetrachloride corresponded to the molar proportion of 8 pounds per hour of magnesium. In this way the gas flow was maintained at the optimum value so that sufficient magnesium was drawn in to give practically complete reduction of the titanium tetrachloride during its passage through the reaction zone. Optimum conditions will obviously depend on maintaining the correct adjustment of nozzle diameter, venturi throat diameter, distance of the nozzle above the venturi and rate of argon flow and magnesium evaporation which require previous calculation and trial but it was found that with the apparatus used the evaporation of magnesium metal may vary between 6 and 18 pounds per hour and the molar proportion of titanium tetrachloride is introduced to correspond to the predetermined rate of magnesium evaporation. Under the conditions stated, the product is delivered as a fine discrete powder, the particle size of which was measured for one experiment and found to 100 vary between $1/12,000$ of an inch and $1/400$ of an inch.

It was also found that with the dimensions given above, anything under 2 cubic feet per minute of argon gave rise to a solid matrix, 105 and anything above 7 cubic feet per minute tends to give only partial reduction or scatters the product too rapidly in the apparatus to permit of easy cleansing of the argon.

It has been found that an electrostatic or 110 cyclone precipitator interposed in the argon circulating system is very effective in collecting the products of reaction and for the purpose of cleansing the argon from minute dust particles which it entrains. 115

What we claim is:—

1. A process for the production of pure titanium or zirconium which comprises reacting the tetrachloride of the required metal in the vapour phase and in the presence of a 120 moving inert gas with the vapour obtained by volatilizing magnesium, and passing the reaction products while entrained in the inert gas through a zone sufficiently cool to solidify the magnesium chloride before the particles 125 are allowed to settle.

2. A process as claimed in Claim 1, wherein the inert gas employed is argon.

3. A process as claimed in Claim 1 or Claim 2, wherein the inert gas is employed as a 130

vehicle to carry one or both of the reaction ingredients into the reaction zone and to carry the reaction products away therefrom.

4. A process as claimed in Claim 3, wherein the inert gas is employed as a vehicle to carry the magnesium vapour forward through a venturi and into a reaction vessel to meet a current of titanium or zirconium tetrachloride vapour.
- 10 5. A process as claimed in any one of the preceding claims, wherein the process is carried out in a closed cycle by passing the inert gas continuously through a jet above a venturi throat arranged in the top of the reaction vessel situated in an outer vessel containing the boiling magnesium and by passing the titanium or zirconium tetrachloride into the reaction vessel below the venturi, the reaction products being removed from time to time through an argon lock from a collecting vessel situated below the reaction vessel and the inert gas being circulated through a condensing system to separate any titanium or zirconium tetrachloride and then re-cycled.
- 15 6. A process for the production of pure titanium or zirconium, substantially as described with reference to the accompanying drawing.

7. Pure titanium or zirconium whenever produced by the process as claimed in any one of the preceding claims.

8. Apparatus for carrying out the process

claimed in any one of Claims 1 to 6, comprising an upright reaction vessel of substantially greater height than width, the upper part of which is surrounded by a closed outer vessel for holding boiling magnesium, said reaction vessel converging at the top above the level of the molten magnesium in the outer vessel in a venturi throat and disposed centrally above the latter, an inlet pipe passing through the cover of the outer vessel and terminating in a nozzle, said inlet pipe being connected to a supply of argon, the said reaction vessel being also provided with an inlet for titanium or zirconium tetrachloride passing through the sides of the outer vessel and the reaction vessel and terminating within the latter at a point below, the venturi throat, the lower part of the reaction vessel opening into a cooling vessel and receiver, the said cooling vessel or the receiver being provided with an outlet for carrying away argon and excess titanium or zirconium tetrachloride.

9. Apparatus for carrying out the process claimed in any one of Claims 1 to 6, substantially as described with reference to the accompanying drawing.

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PROVISIONAL SPECIFICATION

Improvements in or relating to the production of Pure Titanium and Zirconium

- We, JOSEPH PEPPO LEVY, a Turkish Citizen, of 1, Kathleen Avenue, Acton, London, W.3, DAVID HARRY PICKARD and LIONEL PICKARD, both British Subjects, and both of 223, St. John Street, London, E.C.1, do hereby declare this invention to be described in the following statement:—

This invention relates to the production of titanium and zirconium metals in a high state of purity.

- Titanium and zirconium are readily produced in the form of volatilizable chlorides by direct reduction of their ores with carbon in the presence of chlorine, but the production of the pure metals from the chlorides is a matter of considerable difficulty owing to the great affinity of the metals for other substances, more particularly for their affinity for both the oxygen and nitrogen of the atmosphere and carbon and hydrogen as reducing agents. Even traces of impurities, particularly oxygen and nitrogen, may render the metals brittle and unworkable and of much less commercial value, although the metals are of great utility when in the pure condition.

- Many processes have previously been suggested for obtaining pure titanium from the

tetrachloride. Thus it has been previously suggested to obtain titanium by reacting magnesium with titanium chloride in accordance with the formula $2\text{Mg} + \text{TiCl}_4 = 2\text{MgCl}_2 + \text{Ti}$ by introducing the titanium chloride vapour into molten magnesium, titanium being retained in a matrix of unreacted magnesium and magnesium chloride. It is extremely difficult, however, if not impossible, to remove all occluded titanium tetrachloride vapour, and in the subsequent leaching of the mass with hydrochloric acid to remove unreacted magnesium, this residual tetrachloride vapour is hydrolysed, giving titanous acid. Moreover the leaching itself is a difficult operation to carry to completion and the titanium obtained by this process usually contains at least 1% of impurities, mainly because of the difficulty of leaching the solid matrix. The use of hydrochloric acid may also introduce fresh impurities, since the hydrogen liberated may also form titanium hydride and impurities in the steel normally used for lining the chamber may introduce further impurities, especially carbon, which contaminate the titanium.

It has now been found that titanium and

zirconium can be produced in a high state of purity without encountering the difficulties above referred to if the reaction is carried out in the vapour phase in the presence of an inert gas (viz. one of the noble gases, in particular argon, helium or neon, on account of their availability) to act as an entrainment and effect the rapid removal and separation of the products of reaction.

10 It will be shown hereinafter that the employment of a vapour phase reaction in conjunction with an inert gas entrainment not only avoids the difficulties hitherto encountered in obtaining pure titanium or zirconium, but also carries with it many advantages which could not have been foreseen.

Accordingly, in its broadest aspect the present invention includes the process for the production of pure titanium or zirconium which comprises reacting the tetrachloride of the required metal entirely in the vapour phase and in the presence of an inert gas, with magnesium vapour and separating mechanically the titanium or zirconium metal particles formed from the magnesium chloride.

25 The inert gas serves as a vehicle to carry the vapours forward so that when the latter react there is no interruption to the forward movement. The importance of this will be seen when describing the invention specifically.

30 The inert gas employed may conveniently be argon on account of its availability.

The higher temperature of reaction provides a condition of greatly increased chemical activity. Moreover by reducing the tetrachloride with a metal vapour the reaction becomes practically quantitative because at that temperature the products of reaction Ti or $Zr + MCl_2$ ($M =$ reducing metal) are in the solid and liquid phases respectively and can thus be separated by physical means. This removal of the reaction products as rapidly as they are formed ensures that the reaction proceeds to completion and all the metal vapour

is consumed, leaving no residual matrix to be dissolved out as is the case when conducting the reduction in the liquid phase. Furthermore the vapour phase reaction using an entraining gas enables a continuous process in a closed cycle to be carried out.

The magnesium chloride may be submitted to electrolysis, being in the anhydrous condition, and the magnesium formed may be returned to the process and the chlorine used for preparing fresh tetrachloride.

60 It will be appreciated that in view of the affinity of all the metals concerned for both oxygen and nitrogen it is necessary to replace all air in the apparatus by the inert gas before commencing the operation.

The products obtained by the process of the invention are of exceptional purity, partly for the reasons already given, and partly because the employment of an inert gas maintains an inert atmosphere in the apparatus so that there is no detrimental action on the walls of the apparatus or on the products of reaction, as is the case in a liquid phase reaction. Moreover impurities which may be contained in the reducing metal employed, or which it may pick up from the containing vessel, will be left behind in the latter, and parts of the apparatus which would come in contact with hot tetrachloride vapour would be likely to suffer from corrosion, whereas by diluting this vapour with an inert gas this is avoided.

70 It is also a substantial advantage of the process of the invention that the magnesium chloride is obtained in a form in which it can be immediately recovered instead of in the form of a solution which may be too expensive to recover economically and yet be otherwise difficult to dispose of.

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Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1955.

Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

